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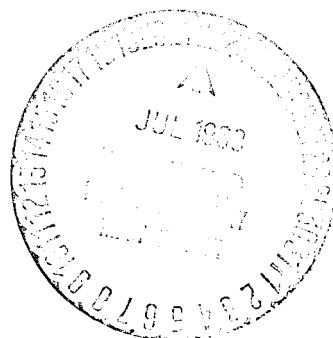
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## DETERMINATION OF RHENIUM IN RHENIUM -- TUNGSTEN ALLOYS

Teiji Okubo and Masao Kojima\*

**ABSTRACT:** Spectrophotometric determination of rhenium according to thiourea method has been applied to rhenium-tungsten alloy. A sample of the alloy was fused with a mixture of sodium carbonate and potassium nitrate, and it was dissolved in water and then diluted. An aliquot of the solution containing 0.1 ~ 2.0 mg of rhenium is taken in a volumetric flask and it is diluted to 100 ml, after 0.2 g of urea, 10 ml of 50% citric acid solution, 25 ml of concentrated hydrochloric acid, 12 ml of 5% thiourea solution and 6 ml of 1 M stannous chloride in 4 M hydrochloric acid solution being added, more than 50 minutes later, the absorbance is measured at 380 m $\mu$ . The method can be applicable to the rapid determination of rhenium in rhenium-tungsten alloy without separating any rhenium from a large quantity of tungsten.

## 1. Introduction

Several different methods have been tested for the determination of the rhenium content in rhenium -- tungsten alloys. One of these is colorimetric analysis with  $\alpha$ -furyldioxime subsequent to the anodic oxidation of the test sample, dissolution, and extraction of the rhenium with methyl ethyl ketone [1]. Another method is colorimetry with thiocyanic acid following decomposition of the sample with nitric acid -- hydrofluoric acid, dissolution in ammonia water, and the isolation of the rhenium by ion exchange [2]. Additional colorimetric methods are decomposition in a similar way with nitric acid -- hydrofluoric acid, dissolution in sodium hydroxide solution, and masking the tungsten with tartaric acid, without decomposing the alloy [3]; as well as calcination of the test sample followed by alkali fusing, then masking the tungsten with citric acid, and the accomplishment of the analysis with dimethylglyoxime [4]. In all of the above procedures, however, the operations entailing decomposition and dissolution are quite complicated. Masking of the tungsten with tartaric or citric acid is a useful rapid analysis technique, and colorimetry with thiocyanic acid, or a  $\alpha$ -furyldioxime, is highly sensitive and is generally applied in analysis for minute quantities of rhenium. It is not believed, however, that these techniques are suitable for the analysis of the alloy as it is normally composed, owing to problems of accuracy. Further, when the test samples are thermally oxidized in the presence of air or oxygen at 500°C, [4], it is known that the highly stable oxide of rhenium,

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rhenum heptoxide, has a high vapor pressure and sublimates at 300°C, or more, [5], and it is believed that this property will cause a negative deviation. In the method previously reported by the writers [6] for the determination of rhenum with thiourea, no effects of the nitrite ion have been observed. If the nitrite ions, which are formed during fusing, are dissociated with urea, fusing may then be accomplished with sodium carbonate -- potassium nitrate, then the tungsten blocked and masked by the addition of citric acid. This method was applied in the rapid determination of the rhenum content in rhenum -- tungsten alloys and the completely satisfactory results obtained are reported below.

## 2. Test Materials and Equipment

### 2.1 Test Materials

50% citric acid solution: 500 ml of the solution was prepared by dissolving 250 g of reagent grade citric acid in water.

Tungsten solution: 500 ml of a solution of 9.0 g of sodium tungstate in water was prepared. 1 ml of the solution contained approximately 10 mg of tungsten.

Urea, anhydrous sodium carbonate, and potassium nitrate: Reagent grades were used.

The other materials were all as previously reported [6].

### 2.2 Equipment

All equipment was as previously reported [6].

## 3. Experiments and Results

### 3.1 Analytical Operations

100 mg of the test sample was refined and placed in a platinum crucible. A mixture of 3 g of powdered sodium carbonate and 1 g of powdered potassium nitrate were added and the mixture was then gradually heated and fused. When the fusing agent melted, there was a violent reaction as the test sample became oxidized. (Owing to the extreme emission of heat, care is required to prevent penetration of the test sample into the crucible should this step become protracted over a lengthy period of time.) After cooling, the product was dissolved in water to give 250 ml of the solution. A portion of the test solution was taken in an amount containing 0.1 -- 2.0 mg of rhenum and placed in a 100 ml measuring flask. 10 ml of a mixture of 50% citric acid solution and 0.2 g of powdered urea were added. The mixture was then agitated until the urea had dissolved. 25 ml of concentrated hydrochloric acid, 12 ml of a 5% thiourea solution and 6 ml of a 1 M stannous chloride -- 4 M hydrochloric acid solution were added. Water was then added to give a total volume of 100 ml. The mixture was then well mixed and allowed to settle for 50 minutes

or more until coloring was completed. The absorbance at 390 mμ was then measured and the quantity of rhenium calculated on the basis of a previously prepared reference line.

### 3.2 Tests of the Methodology

**3.2.1 Quantity of Citric Acid:** When a coloring reaction is attempted without the addition of citric acid, the tungsten precipitates out as a blue colored oxide, turning the solution cloudy blue. Even though a large proportion of the precipitant is filtered out, a very low level of absorption is evinced because the rhenium is filtered out at the same time. However, the formation of the blue oxide can be prevented by adding citric acid. A study was therefore made of the quantity of tungsten present, and the quantity of citric acid required to mask it.

The color reaction was tested by adding citric acid in varied quantities to a solution which contained 1 mg of rhenium and 5 -- 100 mg of tungsten. The observed precipitation of the blue oxide one hour and 20 hours following the preparation of the solution was as given in Figure 1. It was possible to prevent the formation of the precipitant by the addition of 3 ml or more of a 50% citric acid solution per 10 mg of tungsten. The effects of as much as 100 mg of tungsten were nullified when 30 ml of citric acid was added, and it was still possible to make a colorimetric analysis. Further, no effects on the time required for the determination of the absorption curve, absorbance, and coloring of the rhenium thiourea mixture were observed to have been caused by the addition of the citric acid.

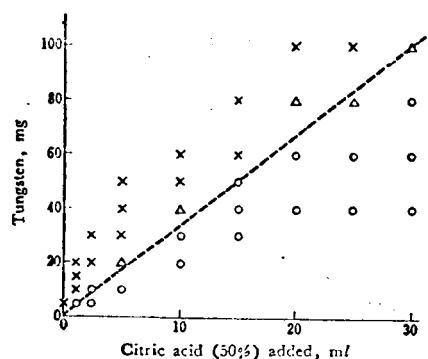


Figure 1. Masking Power of Citric Acid for Tungsten.

**3.2.2 Effects of the Nitrite Ions, and the Quantity of Urea Required to Offset Them:** When the test material is fused with sodium carbonate -- potassium nitrate, nitrite ions are formed as a result of the decomposition of the nitrate. This effect blocks the coloring of the rhenium. The effects of the nitrite ions on the absorbance of rhenium, when a solution of potassium nitrite was added to a solution containing 1 mg of rhenium and 20 mg of tungsten and the coloring reaction described in paragraph 3.1 was induced without the addition of urea, were as given in Figure 2.

Since a very small number of nitrite ions will cause a negative deviation, it was decided that urea should be added to dissociate them. When a coloring reaction was induced in a mixture of 10 ml of a 0.1M potassium nitrite solution and a solution of 1 mg of rhenium, only about one-half of the usual absorbance was evidenced when 50 mg of urea was added. However, when 100 mg of urea, or more, was added, it became apparent that the effects of the nitrous acid were completely overcome. Further, when 10 mg of metallic rhenium and

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100 mg of tungsten were prepared and fused in accordance with the methodology described in 3.1, above, and 1/10 of this quantity taken for a test, the absorbance, when urea was not used, was about 1/3 of that which should be anticipated. However, when 50 mg, or more, of urea was used, absorbance normalized and the expected value was read. For this reason, it is obvious that the nitrite ions formed during fusing are completely eliminated. When 2 g of urea was added, no effects on the absorption curve or on absorbance were observed.

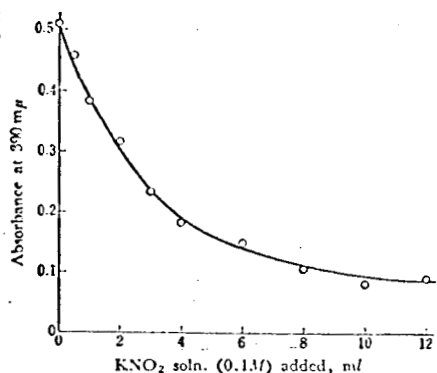


Figure 2. Effect of Nitrite Ion.

### 3.2.3 Tests With Synthesized Materials:

5 -- 50 mg of metallic rhenium powder were prepared and powdered metallic tungsten added to this in an amount of about 100 mg in order to synthesize a test sample. The analytical values obtained through the operations described in paragraph 3.1, above, were as given in Table 1.

The deviations during spectrographic analysis were minor, and it is believed that the synthesized sample was equivalent to the actual alloy.

### 3.3 Analysis of the Actual Test Material

Ten tests were made following the procedures described in paragraph 3.2.3, using about 80 mg of prepared thermocouple type 26% rhenium -- tungsten alloy. The measurement results were in every case  $25.6 \pm 0.6\%$ , giving a standard deviation of 0.3%.

Table 1. Analytical Test

Rhenium taken (mg)	Tungsten taken (mg)	Rhenium	
		Determined (mg)	Error (mg)
5.18	91.43	5.23	+0.05
10.30	93.66	10.38	+0.08
15.62	81.11	15.63	+0.01
20.95	80.75	21.05	+0.10
29.74	68.39	30.2	+0.46
41.57	61.72	41.4	-0.17
49.22	52.68	49.5	+0.28

### 4. Conclusions

As the above results make clear, it is possible to make a hasty, yet accurate, determination of the rhenium content in the recently much demanded rhenium -- tungsten alloys by the above described method. The impurities in the usual rhenium -- tungsten alloys are so minor that they may be disregarded, but it is not possible to apply this

method to alloys containing molybdenum and palladium, which, as it has been reported, mask the rhenium.

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